

**This Page Is Inserted by IFW Operations
and is not a part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- **BLACK BORDERS**
- **TEXT CUT OFF AT TOP, BOTTOM OR SIDES**
- **FADED TEXT**
- **ILLEGIBLE TEXT**
- **SKEWED/SLANTED IMAGES**
- **COLORED PHOTOS**
- **BLACK OR VERY BLACK AND WHITE DARK PHOTOS**
- **GRAY SCALE DOCUMENTS**

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problems Mailbox.**

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau**COPY**

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C22B 3/08, 19/02, 11/00, 23/00, 15/00	A1	(11) International Publication Number: WO 96/29439
		(43) International Publication Date: 26 September 1996 (26.09.96)
(21) International Application Number: PCT/AU96/00157 (22) International Filing Date: 22 March 1996 (22.03.96) (30) Priority Data: PN 1913 22 March 1995 (22.03.95) AU (71) Applicants (for all designated States except US): M.I.M. HOLDINGS LIMITED [AU/AU]; 410 Ann Street, Brisbane, QLD 4000 (AU). HIGHLANDS GOLD PROPERTIES PTY. LIMITED [PG/PG]; 9th floor, Pacific Place, Cnr. Champion Parade and Musgrave Street, Port Moresby (PG). (72) Inventors; and (75) Inventors/Applicants (for US only): HOURN, Michael, Manthaw [AU/AU]; 14 Kinrade Place, Carindale, QLD 4152 (AU). TURNER, Duncan, William [AU/AU]; 89 Albion Road, Albion, QLD 4010 (AU). HOLZBERGER, Ian, Raymond [AU/PG]; Section 40, Lot 29, Unit 1/3 Justice Street, Port Moresby (PG). (74) Agent: CULLEN & CO.; Level 12, 240 Queen Street, Brisbane, QLD 4000 (AU).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.
(54) Title: ATMOSPHERIC MINERAL LEACHING PROCESS		
(57) Abstract <p>The present invention relates to a method of processing a sulphide mineral composition which at least partly comprises an iron containing mineral, the method comprising the steps of: (a) milling said composition to a particle size P80 of 20 microns or less; (b) leaching said composition with a solution comprising sulphuric acid and ferric ions at ambient pressure whilst sparging with an oxygen containing gas in an open tank reactor at a temperature of up to about the boiling point of the solution, whereby at least some of the acid and at least some of the ferric ions are obtained from dissolution of the iron containing mineral, and ferrous ions generated by the leaching reaction are substantially re-oxidised to ferric ions in the leaching solution; (c) precipitating excess iron and separating said iron together with any solid materials from the leaching solution; (d) extracting desired metal ions from the leaching solution by solvent extraction with an organic solvent, such that the raffinate comprises sulphuric acid and ferric ions; (e) returning the raffinate to the leaching tank and blending with further milled composition; (f) separating the metals from the organic phase obtained in step (c) by stripping with electrolyte and electrowinning.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

TITLE

ATMOSPHERIC MINERAL LEACHING PROCESS

FIELD OF THE INVENTION

This invention relates to a method of enabling
5 a sulphide mineral composition to be leached at
atmospheric pressure instead of above atmospheric
pressure which has been hitherto required in order to
achieve acceptable rates of leaching.

BACKGROUND ART

10 Sulphide minerals such as copper, nickel, zinc,
gold and the like are recovered from their ores by a
number of well known processes. One such process uses the
relative solubility of the mineral in solution to allow
the mineral to be leached from the ore. Conventional
15 leaching processes require expensive equipment and a high
level of technical expertise to maintain and use the
equipment. Thus, it is not uncommon for an oxidative
hydrometallurgy leaching plant to be located some
distance away from the ore body and even in another
20 country. This in turn significantly increases
transportation costs, and it should be realised that
transportation of ore or only partially enriched ore
containing perhaps only a few percent of the desired
mineral is extremely wasteful and undesirable, but in the
25 absence of being able to recover the metal of value from
the minerals on-site, there is little real alternative.

The processing methods of oxidative
hydrometallurgy are commonly used in many different
applications. Due to the refractory nature of many of
30 the mineral species treated in such processes, these
applications generally require leaching conditions of
high temperature and pressure and require substantial
supplies of oxygen. For example, base metals such as
copper, nickel and zinc can be recovered by
35 hydrometallurgical processes which usually embody
pretreatment, oxidative pressure leaching, solid/liquid
separation, solution purification, metal precipitation or
solvent extraction and electrowinning.

According to conventional technology, oxidative leaching processes usually require very aggressive conditions in order to achieve acceptable rates of oxidation and/or final recoveries of metal. Under these conditions, which often mean temperatures in excess of 150°C or alternatively temperatures in the range 150 - 200°C and total pressures in excess of 1500 kPa, the chemical reactions which occur use large quantities of oxygen, both on stoichiometric considerations and in practice where amounts in excess of stoichiometric requirements are used due to process inefficiencies.

An example of oxidative hydrometallurgy is the treatment of refractory gold ores or concentrates. Refractory gold ores are those gold ores from which the gold cannot readily be leached by conventional cyanidation practice. The refractory nature of these gold ores is essentially due to very fine (sub microscopic) gold encapsulated within the sulphide minerals. This gold can often only be liberated by chemical destruction (usually oxidation) of the sulphide structure, prior to recovery of the gold, which is usually done by dissolution in cyanide solution. Of course, other lixiviates such as thiourea and halogen compounds and the like may also be used.

A number of processing options are available for treating refractory gold ores which contain sulphide minerals like pyrite, arsenopyrite and others. Pressure oxidation, typified by the so-called Sherritt process, is one such process which typically consists of the steps of feed preparation, pressure oxidation, solid/liquid separation, liquid neutralisation and gold recovery from oxidised solids usually by cyanidation.

A cryogenic oxygen plant is usually required to supply the substantial levels of oxygen demand during the pressure oxidation step, which is the heart of the Sherritt process. Typically, the conditions for the pressure oxidation step require temperatures in the region of 150°C to 210°C, a total pressure of 2100 kPa, a

pulp density equivalent to 20% to 30% solids by mass, and a retention time of two hours to three hours.

The typical oxidative hydrometallurgical processing methods referred to above generally have oxidation reactions that are carried out in multicompartment autoclaves fitted with agitators. In order to withstand the generally highly aggressive conditions of the reactions, the autoclaves are very costly, both to install and maintain. These vessels must be capable of withstanding high pressure, and linings of heat and acid resistant bricks need to be used. The agitators are made of titanium metal, and the pressure relief systems utilised are also costly and require high maintenance. These high costs and the sophistication of the technology (skilled operators are generally required) detract from the wider acceptance of high pressure/high temperature oxidation, particularly for use in remote areas or by small to medium size operators.

Cooling of the agitators also presents problems, and expensive cooling coils and heat exchange jackets are required to keep the leach temperature at optimum conditions.

The aggressive leaching conditions outlined for recovery of metal values from base metal concentrates are required to achieve acceptable leaching rates from the minerals. Under conditions of atmospheric pressure, the leaching rates of the mineral species are too low to support an economically viable leaching process.

Attempts have been made to reduce the aggressive conditions and to lower the pressures in order to lower the cost in building and operating a leaching plant. For instance, it is known to initially fine grind the ore or the ore concentrate (it being known to use flotation as an initial step to concentrate minerals in the ore), prior to oxidative hydrometallurgy to leach the ore. The fine grinding increases the surface area to volume ratio of the ore particles to improve extraction. A fine grind to an 80% passing size of 15 micron or less

is used. The initial fine grind does result in acceptable leaching rates being observed with less aggressive conditions, and leaching can be carried out at temperatures of 95 - 110°C and at a pressure of about 10 atmospheres or about 1000 kPa.

Thus, while some progress has been made in reducing the operating parameters and thus the cost of the leach system to date, the leach still must be carried out under pressurised conditions. Pressure leach systems are expensive to build. Because of the high capital and processing costs of pressure leach systems, these systems are economical only for high grade concentrates. High grade concentrates are required because -

- (1) operating cost per unit of contained metal considerations
- (2) less heat generation/exchanger problems with high grade concentrates
- (3) capital cost per unit of contained metal is lower balancing up with large initial capacity outlay to metal recovery.

It is also known to oxidatively leach sulphide mineral species with ferric ions. Ferric ion is a relatively effective oxidising agent which enables oxidation to be carried out at pressures less than that normally required when oxygen is the oxidant. However, there are a number of practical difficulties associated with using ferric ions as the oxidant. First, at ambient pressure the reaction is inherently slow. Also during the leaching reaction, ferric ions are reduced to ferrous ions. A build up of ferrous ions in the leaching solution adversely affects the rate of leaching. Also the ferrous ions must normally be removed from the leach liquor prior to further processing which is difficult.

Leaching solutions are generally recycled. However, before a ferric leaching solution can be recycled the ferrous ions must be re-oxidised to ferric ions. This is because it is important for maximum effectiveness of the leach that most of the iron is in

the ferric form. The leach solutions can be regenerated by electrolytic oxidation, use of strong oxidisers such as permanganate, oxidation under high pressure of oxygen, or oxidation by bacteria. Each of these methods suffer from disadvantages which limit their application. For example high pressure oxidation is limited by the costs of the autoclaves involved. Oxidation by oxygen under ambient pressure can occur but only at an inherently slow rate. Catalysts may be used to increase the rate but such catalysts are expensive and are not economical for recovery from low grade ores.

Each of the above processes either require expensive autoclaves or other equipment and/or the addition of expensive reagents used for oxidation or regeneration of ferric ions. This means that it is only economically viable to process high grade ores by these methods. Another disadvantage of these processes is that they generate significant amounts of waste products such as gypsum, sulphuric acid and jarosite. These products must be disposed of in an environmentally acceptable manner which also adds to the cost.

Many valuable copper or zinc bearing ores are found in association with iron containing ores such as pyrite. Pyrite is of little value and is effectively a diluent of the valuable ores. Further, leaching of pyrite produces iron species which interfere with extraction of the desired metals. Pyrite is therefore generally removed from other ores prior to processing. The pyrite may be removed by methods such as flotation. Such separation also adds significantly to the cost and in some cases it is not economically feasible to process some low grade ores at all.

OBJECT OF THE INVENTION

It is an object of the present invention to provide a method of processing a mineral composition which can be carried out under mild conditions of temperature and pressure and which is economical when compared with existing processes.

The present inventors have surprisingly discovered that by subjecting sulphide mineral compositions to fine grinding prior to leaching under conditions in which the solution chemistry is controlled in a particular manner, such compositions can be processed under ambient conditions in open reactors without the need for the addition of expensive reagents and a separate step for regeneration of the leaching solution.

10 According to a first embodiment of the present invention there is provided a method of processing a sulphide mineral composition which at least partly comprises an iron containing mineral, the method comprising the steps of;

15 (a) milling said composition to a particle size P80 of 20 microns or less,

(b) leaching said composition with a solution comprising sulphuric acid and ferric ions at ambient pressure whilst sparging with an oxygen containing gas in an open tank reactor at a temperature of up to about the boiling point of the solution, whereby at least some of the acid and at least some of the ferric ions are obtained from dissolution of the iron containing mineral, and ferrous ions generated by the leaching reaction are substantially re-oxidised to ferric ions in the leaching solution;

25 (c) precipitating iron and separating said iron and solid materials from the leaching solution;

(d) extracting desired metal ions from the leaching solution by solvent extraction with an organic solvent to form an organic phase and raffinate comprising sulphuric acid and ferric ions;

30 (e) returning the raffinate to the open tank reactor and blending with further milled composition;

(f) separating the metals from the organic phase obtained in step (d) by stripping with electrolyte from an electrowinning cell and electrowinning.

According to a second embodiment of the present invention there is provided a method of processing a

sulphide mineral composition which at least partly comprises an iron containing mineral, the method comprising the steps of;

5 (a) milling said composition to a particle size of P80 of 20 microns or less and

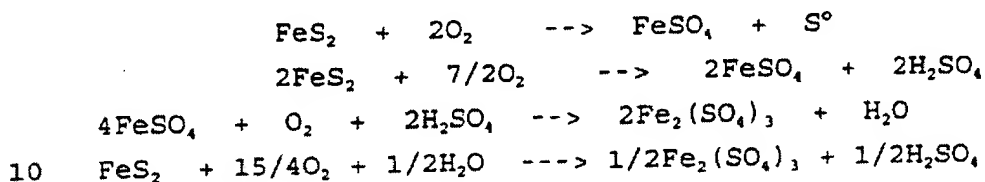
(b) leaching said composition with a solution comprising sulphuric acid and ferric ions at ambient pressure whilst sparging with an oxygen containing gas in an open tank reactor at a temperature of up to about the boiling point
10 of the solution, whereby at least some of the acid and at least some of the ferric ions are obtained from dissolution of the iron containing mineral, and ferrous ions generated by the leaching reaction are substantially re-oxidised to ferric ions in the leaching solution.

15 According to a third embodiment of the present invention there is provided a method of processing a metal sulphide flotation concentrate comprising the steps of;

(a) milling said ore to P80 of 5 micron and
20 (b) leaching said ore with a solution comprising sulphuric acid and ferric ions, at ambient pressure whilst sparging with an oxygen containing gas in an open tank reactor at a temperature of up to about the boiling point of the solution.

25 The method of the present invention is applicable to any type of sulphide mineral composition. Such compositions include ores and concentrates. The method of the present invention is especially suitable for processing concentrates. Examples of suitable
30 materials include chalcopyrite, bornite, enargite, pyrite, covellite, sphalerite, chalcocite, pentlandite, cobaltite, pyrrhotite or mixtures of any two or more thereof. Metals which can be extracted from the mineral compositions according to the method of the first
35 embodiment include copper, zinc, nickel and cobalt. The concentrate grade may range from very low such as for example with copper containing materials 7-8 wt% copper to high grade concentrates having about 26 wt% copper.

The iron containing mineral can be any mineral which under the leaching conditions will produce ferrous or ferric ions upon dissolution. Especially preferred is pyrite, FeS_2 , or pyrite ore which produces ferric ion and some sulphuric acid according to the following:



Preferably sufficient iron containing mineral is present such that it provides substantially all of the ferric ions in the leaching solution. The relative amounts of iron containing mineral will of course depend on the types and amounts of the other components in the ore. Typically about 20 to about 60wt% pyrite is present. If desired, additional pyrite or other minerals may also be added. Alternatively additional ferric sulphate may be added. It can be seen that the iron containing minerals may also provide a source of sulphuric acid. Additional acid may need to be provided if required. Sulphuric acid is typically generated in associated processes such as electrowinning and solvent extraction. Preferably sulphuric acid produced in this way is recycled to the leaching step.

A preferred type of apparatus which may be suitable for producing fine or ultra fine sulphide mineral compositions in finely divided form is a stirred mill. However, it will be appreciated that other types of comminution apparatus may also be used such as wet and dry vibratory mills or planetary mills to provide the fine or ultra fine milling of the invention.

In a preferred form, vertical or horizontal stirred mills generally consist of a tank filled with small diameter grinding media (for example 1 - 6 mm diameter steel or ceramic balls) which are agitated by means of a vertical or horizontal shaft usually fitted

with perpendicular arms or discs. The sulphide minerals (usually contained in the form of a concentrate) are milled by the sheering action produced by ball to ball contact, or between balls and the stirrer or balls and the walls of the tank. The milling may be carried out dry or wet. These vertical or horizontal stirred mills have been found to be satisfactory in providing the required degree of fineness, and in satisfying energy and grinding media consumption requirements. Furthermore, the activity of the ground product as measured by its response to subsequent oxidation, has also found to be satisfactory. In this respect the ore is ground to a maximum average particle size of 80% passing size of 20 microns as measured with a laser sizer. Preferably the particle size is less than P80 of 5 micron. The desired particle size may vary with the type of mineral species used. Especially preferred particle sizes for different concentrates, expressed as P80, are

chalcopyrite/bornite - 4.5 micron; enargite - 3 micron; pyrite - 3 micron; covellite - 20 micron; chalcocite - 20 micron; pentlandite - 5 micron and cobaltite - 5 micron.

The mild conditions of pressure and temperature in the oxidative leach that follows the milling, are low when compared with the relatively high pressure and temperature conditions of known pressure oxidation techniques such as the Sherritt process or Activox process. As indicated above, the Sherritt process typically requires temperatures in the order of 150 to 210°C and total pressures in the order of 2100 kPa. The Activox process is designed to operate at pressures between 9 and 10 atmospheres and temperatures within the range 90 - 110°C. However, the acceleration of the leaching response of the mineral species in accordance with the present invention allows the oxidative leach to be conducted at temperatures below about 100°C and at atmospheric pressure in cheap open tank reactors.

With the preferred operating conditions being at about 60°C up to the boiling point of the solution and

at 1 atm total pressure, a low cost reactor such as an open tank is sufficient to serve as the leaching vessel. There also is no need for the use of expensive titanium metal agitators due to the less corrosive nature of the leach solution. Furthermore, abrasion problems are substantially reduced due primarily to the fine nature of the feed.

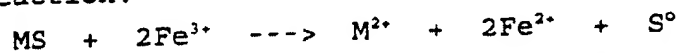
Importantly, the complex heat exchange and pressure let down systems necessary for operation of a pressure vessel are not necessary as the reactor operates at atmospheric pressure. Excess heat is removed from the system through solution evaporation and this removes the need for costly heat exchange facilities. Also the reaction becomes autogenous at above about 60 to about 70°C. If additional heating is required this can be easily done by known methods such as the injection of steam.

Further, much higher percent solids slurries can be treated by the described method due to the relaxation of the requirements for low sulphur levels in feed to an autoclave necessary for heat control purposes. Typically the leach slurry density varies from about 10 to about 20 wt%.

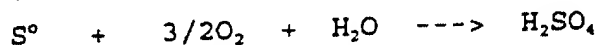
In the method of the first embodiment the leaching solution is typically recycled raffinate from the solvent extraction step. In this case preferably most of the ferric ion and sulphuric acid may be generated by the leach/solvent extraction/electrowinning process. If the leach is not part of a continuous process, ferric and sulphuric acid may be added if required. Typically the raffinate comprises 30 - 40g/lH₂SO₄ and 10 - 20g/l Fe. The Fe will normally be present as a mixture of ferric and ferrous ions.

The leaching solution is sparged with an oxygen containing gas. The gas may be air or preferably oxygen or oxygen enriched air. The gas flow is dependent upon the amount of oxygen required to sustain the leaching reaction and regeneration of the ferric ions. Typically the gas flow is about 400 to about 1000kg O₂ per tonne of

metal produced. If desired a surfactant or the like may be added to minimise frothing of the leaching solution. Under the conditions of the leaching reaction, the metals may be oxidised by ferric ion according to the following general reaction:

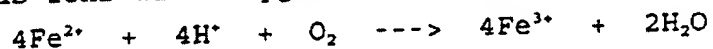


Further oxidation of the elemental sulphur to sulphate according to the reaction:



requires elevated temperature and pressure and does not occur to any significant extent under the leaching conditions of the present invention. For example, at 90°C at atmospheric pressure, in the absence of bacterial catalysis, less than 5% of the elemental sulphur is oxidised to sulphate. By comparison, at 180°C and 12 atmospheres oxygen partial pressure, most of the sulphur is oxidised to sulphate. Oxidation to sulphate has several disadvantages as additional neutralising reagents are required during the postleaching neutralisation steps. A further advantage of formation of elemental sulphur is that gaseous emission such as sulphur dioxide is minimised which causes an environmental hazard. Further by not carrying out the oxidation completely to sulphate, the consumption of oxygen is significantly reduced which saves on operating costs. For example conventional PSA oxygen plants may be sufficient to supply the oxygen without the need for cryogenic oxygen plants. This in turn reduces the capital cost and the operating costs by using simple to operate equipment.

The ferric ions are regenerated by reaction of the ferrous ions with oxygen according to:



Typically oxidation of the ferrous ion occurs at a rate of 2 - 5g of ferrous ion oxidised per litre of slurry per hour of reaction.

After substantially all the mineral has been oxidised the leach slurry may be further processed according to known methods. Preferably the slurry is

filtered to remove solids and the clear liquid subjected to solvent extraction followed by electrowinning. Typically the leach slurry is neutralised prior to any further processing. As described above the production of sulphate is reduced under the conditions of the present invention, thereby minimising the amount of neutralising agents which need to be added. Typically the slurry is neutralised by the addition of limestone or the like. This also precipitates excess iron, arsenic and other impurities generated in the leach. Tests carried out under the conditions of the present invention have also indicated that iron can be selectively precipitated and remains in the leach residue as goethite, jarosite or some form of hydrated oxide, whilst valuable minerals like nickel, copper or zinc remain in solution. If desired the precipitated solids may be further filtered and any remaining liquid may be returned to the leach solution for further processing. As described above substantially all of the sulphide sulphur is oxidised to elemental sulphur during the leaching reaction. The elemental sulphur is present as finely dispersed granules. Because the leach is conducted at temperatures below the melting point of sulphur ie 120°C, agglomeration of molten sulphur is avoided. The granulated sulphur is normally removed from the leaching solution with the goethite and/or other iron residue.

The solids which are separated from the leaching solution may be further treated to extract any precious metals such as gold, platinum or silver. These methods of extraction such as cyanidation for gold are well known in the art.

The steps of solvent extraction and electrowinning are well known in the art and need not be described in detail. Typically the neutralised slurry may filtered and extracted with an organic solvent which recovers metals such as copper, nickel or zinc. The metals may then be stripped from the organic phase by known methods. The metals are then separated from the

electrolyte by electrowinning. The spent electrolyte may then be returned to the stripping stage.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram of the method according to a preferred embodiment of the invention.

BEST MODE

The present invention will now be described in relation to the following examples. However, it will be appreciated that the generality of the invention as described above is not to be limited by the following description.

Example One - Enargite and Chalcocite Leaching

Copper flotation concentrate containing 19.5% copper, 4.0% arsenic, 23% iron, 2.35 g/t gold and 36% sulfide sulfur was milled to a size of 80% passing 5 micron in a horizontal 1 litre stirred ball mill. Mineralogically the concentrate was composed of 11.9% chalcocite (Cu_2S), 20.9% enargite (Cu_3AsS_4), 50% pyrite (FeS_2) and the remainder was siliceous gangue minerals.

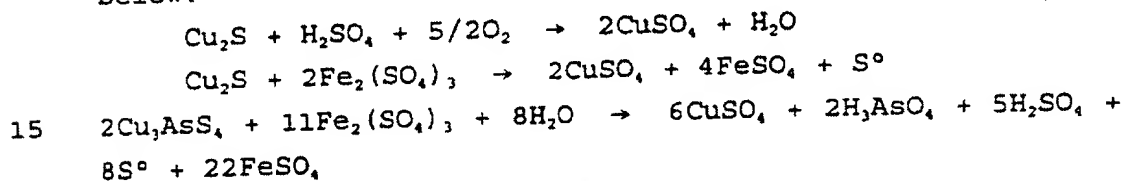
The milled pulp was leached at 90°C in an open reactor utilising a ferric ion sulfuric acid lixiviant solution with either oxygen or air sparging. The solids were recovered by filtration and reslurry washed with 5% v/v sulfuric acid solution, prior to being dried and assayed. Post leach solutions were analysed for copper, arsenic and iron by conventional atomic absorption spectroscopy analytical methods. Ferrous and ferric levels were determined by potassium permanganate titrations, whilst the acid levels were determined by a neutralisation method.

Greater than 92% copper dissolution was achieved from concentrate milled to a particle size of P_{80} 3.5 microns in 10 hours employing leach conditions of 10% pulp density, 30 g/L ferric ions, 50 g/L sulfuric acid, 90°C, oxygen sparging and 2.0 kg/tonne lignosol. Lignosol was used to reduce the amount of frothing in the initial stages of the leach.

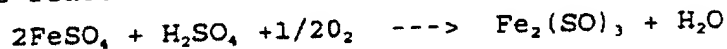
The leach residue was then leached in aerated

sodium cyanide solution to recover gold. The leach test was conducted at ambient temperature with 300ppm free NaCN maintained in the leach solution during the leach. The test was run for 24 hours at a pulp density of 45% solids. Greater than 82% gold extraction was achieved from the residue.

The predominate leaching mechanism thought to be occurring in the above system involves ferric ions acting as the oxidant, although it is conceivable that an acid/oxygen mechanism is also operating. The predominate reactions occurring in this leaching system are presented below.



Ferric iron was regenerated in the leach solution by the action of oxygen on ferrous iron according to the reaction:



In this way, the ferric oxidant was continually regenerated during the leaching process.

The pulp density in the reactor appeared to be limited by the solubility of copper sulfate in the resulting iron/acid electrolyte. The use of air instead of oxygen increased the leaching residence time from 10 hours (oxygen) to 14 hours (air) without loss of overall copper recovery.

Example Two - Chalcocite Leaching

Copper flotation concentrate containing 8.1% copper, 0.2% arsenic, 13.8% iron and 18% sulfide sulfur was milled to a size of 80% passing 5 micron in a horizontal 1 litre stirred ball mill. This concentrate contained 9.4% chalcocite (Cu_2S), 1.3% enargite (Cu_3AsS_4), 29.6% pyrite (FeS_2) and the remainder was siliceous gangue.

The milled pulp was leached at 90°C in an open reactor utilising a ferric ion sulfuric acid lixiviant solution with either oxygen or air sparging. Greater than 95% copper dissolution was achieved in 10 hours employing leach conditions of 10% pulp density, 30 g/L ferric ions, 50 g/L sulfuric acid, 90°C, oxygen sparging and 2.0 kg/tonne lignosol.

Example Three - Chalcopyrite Leaching

Copper flotation concentrate containing 18.0% copper, 25.5% iron and 18.6% sulfide sulfur was milled to a size of 80% passing 5 micron in a horizontal 1 litre stirred ball mill. This concentrate contained 51.8% chalcopyrite (CuFeS_2), 20.8% pyrite (FeS_2) and the remainder was siliceous gangue.

The milled pulp was leached at 80°C in an open reactor utilising a ferric ion sulfuric acid lixiviant solution with oxygen sparging. Greater than 95% copper dissolution was achieved in 10 hours employing leach conditions of 10% pulp density, 5 g/L ferric ions, 20 g/l ferrous iron, 50 g/L sulfuric acid, 90°C, oxygen sparging and 2.0 kg/tonne lignosol.

The method of the invention can be used in association with other upstream or downstream processes. For instance, prior to the fine grind and leach, the ore can be treated in one or more flotation steps. Downstream processes can include flotation processes with or without additional fine grinding, and/or can include solvent extraction and electrowinning steps.

Example Four - Nickel Leaching

Nickel bearing concentrate containing 1.7% nickel, 0.03% cobalt, 11% iron and 16% sulfide sulfur was milled to a size of 80% passing 5 micron in a horizontal 1 litre stirred ball mill. Mineralogically the concentrate was composed of pentlandite, pyrite and the remainder was siliceous gangue materials.

The milled pulp was leached at 90°C in an open reactor utilising a ferric ion sulfuric acid lixiviant solution with oxygen sparging. The solids were recovered

by filtration and reslurry washed with water, prior to being dried and assayed. Post leach solutions were analysed for nickel, cobalt and iron by conventional atomic absorption spectroscopy analytical methods. 5 Ferrous and ferric levels were determined by potassium permanganate titrations, whilst the acid levels were determined by a neutralisation method.

Greater than 92% nickel and 86% cobalt dissolution was achieved from concentrate milled to a 10 particle size P80 of 5 microns in a leach time of 8 hours employing leach conditions of 10% pulp density, 5 g/L ferric ions, 20 g/l ferrous iron, 80 g/L sulfuric acid, 90°C, oxygen sparging and 2.0 kg/tonne lignosol. Lignosol was used to reduce the amount of frothing in the 15 initial stages of the leach.

Example Five - Cobalt Leaching

Cobalt bearing concentrate containing 0.309% cobalt, 8.5% iron and 0.66% arsenic was milled to a size of 80% passing 3 microns in a horizontal 1 litre stirred 20 ball mill. Mineralogically the concentrate was composed of cobaltite and cobaltiferous pyrite, pyrite and the remainder was siliceous gangue minerals.

The milled pump was leached at 90°C in an open reactor utilising a ferric ion sulfuric acid lixiviant 25 solution with oxygen sparing. The solids were recovered by filtration and reslurry washed with water, prior to being dried and assayed. Post leach solutions were analysed for cobalt and iron by conventional atomic absorption spectroscopy analytical methods. Ferrous and 30 ferric levels were determined by potassium permanganate titrations, whilst the acid levels were determined by a neutralisation method.

Greater than 79% cobalt dissolution was achieved from concentrate milled to a particle size of 35 P80 of 3 microns in a leach time of 8 hours employing leach conditions of 10% pulp density, 10 g/L ferric ions, 50 g/L sulfuric acid, 90°C, oxygen sparging and 2.0 kg/tonne lignosol.

Example Six - Zinc Leaching

Zinc concentrate containing 46.6% zinc, 10% iron and 2.8% lead was milled to a size of 80% passing 3 micron in a horizontal 1 litre stirred ball mill.

5 Mineralogically the concentrate was composed of sphalerite, galena, pyrite and the remainder was siliceous gangue minerals.

The milled pulp was leached at 90°C in an open reactor utilising a ferric ion sulfuric acid lixiviant solution with oxygen sparging. The solids were recovered by filtration and reslurry washed with water, prior to being dried and assayed. Post leach solutions were analysed for zinc and iron by conventional atomic absorption spectroscopy analytical methods. Ferrous and ferric levels were determined by potassium permanganate titra-

10
15

tions, whilst the acid levels were determined by a neutralisation method.

Greater than 97% zinc extraction was achieved from zinc concentrate milled to a particle size of P80 of 3 microns in a leach time of 8 hours employing leach conditions of 10% pulp density, 10 g/L ferric ions, 50 g/L sulfuric acid, 90°C, oxygen sparging and 2.0 kg/tonne lignosol.

20

25 Example Seven - Chalcopyrite leaching as a continuous process

The example below describes the operation of a fully continuous pilot plant designed to produce 8 kg per day of LME grade A cathode copper from a copper concentrate. The pilot plant ran for 21 days treating the feed outlined below.

30

Referring to Figure 1 a concentrate sample of the composition listed below was slurried in tap water at a slurry density of 60% w/w. The slurry was then milled in step 1 to a particle size of 80% passing 10 microns in a horizontal stirred bead mill.

35

Table 1 Composition of the concentrate sample:

CuFeS ₂	37% w/w
FeS ₂	44% w/w

18

SiO₂ 11% w/w

Other 8% w/w

The slurry sample was then mixed in step 2 with solvent extraction plant raffinate 3 to dilute the slurry density of 15 % w/w. The raffinate contained 35 g/l H₂SO₄, 9 g/l ferric iron and 10 g/l ferrous iron.

The diluted slurry was then pumped through a three vessel leaching train 4,5,6 at a flow rate designed to give a residence time in the leaching train of 20 hours. The leaching train consisted of three agitated 100 litre baffled tanks. Slurry flowed by gravity from one tank to the next. The tanks were maintained at 90°C by a combination of the exothermic nature of the leach reaction and the injection of live steam into the slurry. Oxygen was injected into the slurry by air spear 7,8,9 located below the leach agitator. The oxygen was added at a rate of 600 kg per tonne of copper produced. The copper extraction across the leaching circuit was 97% w/w.

No acid or iron sulphate was added to the leaching circuit for the duration of the 21 day pilot plant run.

Leached slurry overflowed the final leach tank into a neutralisation tank 10 and then to a thickener 10A. The leach solution composition was typically 17 - 19 g/l copper and 35 - 45 g/l iron. The slurry was neutralised to pH 2.0 with limestone slurry 12 to precipitate iron from the leach slurry as goethite 13. Finely granulated elemental sulphur was removed with the goethite. The slurry comprising the goethite, sulphur and leach residue was filtered 11 and any liquid was returned to the leach solution 14.

Neutralised slurry was then pumped through a plate and frame pressure filter 15. The filtrate contained 17 - 19 g/l copper, 20 g/l iron and 5 g/l H₂SO₄. The filtrate was then pumped through a three stage solvent extraction plant 16,17,18 to recover copper from the leach liquor. The raffinate from the solvent

extraction stage contained 0.3 g/l copper, 20 g/l iron and 35 g/l H_2SO_4 and 20 g/l iron, and was transferred back to the leaching circuit and blended with more ground concentrate at 2.

5 Loaded organic from the solvent extraction plant was then stripped 19 with spent electrolyte containing 180 g/l H_2SO_4 . The stripped organic 20 was pumped back to the extraction stage.

10 The rich electrolyte 21 was then pumped through a 200 litre electrowinning cell 22 containing two cathodes and three anodes. Each cathode face had an area of $0.25m^2$. Copper was plated out from the rich electrolyte at a current density of $280 A/m^2$ to produce a cathode plate. The spent electrolyte from the cell
15 contained 180 g/l H_2SO_4 and 32 g/l copper. The copper cathode was analysed and met the requirements for LME Grade A.

20 The goethite leach residue was leached in sodium cyanide to determine the amount of gold which could be recovered from the oxidised concentrate. The leach residue was leached at 45% w/w solids at pH 10, with a free cyanide level of 300 ppm maintained throughout the leach. The slurry was leached for 24 hours in a batch test. Gold recovery from the leach
25 residue was 92.5% w/w.

30 It can be seen that the methods of the present invention offer a number of advantages over existing methods. The need for tight control on concentrate grade is relaxed due to the lower operating costs of the leach relative to a pressurised leach, and the control of excess heat generation through evaporative cooling of the open tank reactors.

35 The leach can be conducted in cheap open tanks instead of expensive pressure vessels. An equivalent sized pressure leach facility may cost about 6 to 8 times as much as the open tank leaching system of the present invention. This also enables a leaching circuit to be constructed practically on site. This avoids costs of

transportation which can be considerable. In some cases these costs may make it uneconomical to transport and process low grade ores.

5 The leach circuit is less sensitive to grade of metal. Therefore this will enable higher metal recovery in upstream unit operations.

10 The method of the present invention is also capable of producing a high grade electrowin metal. For example in some cases it may be possible to produce a product through solvent extraction/electrowinning which can be sold directly. Smelted metal generally requires further refining. This enables substantial cost savings as well as producing a product which will attract a premium price.

15 The leach reaction is self-sustaining when coupled with a solvent extraction-electrowinning plant, as the only reagents that need to be added to the leach are air/oxygen and a neutralising agent such as lime. The need for addition of expensive reagents is
20 eliminated.

 The present invention is ideal for mineralogically complex ores which are finely disseminated base metal sulphides minerals with other sulfide (e.g. chalcocite, sphalerite, enargite covering
25 pyrite ores) that have been traditionally difficult to treat metallurgically.

 It should be appreciated that various other changes and modifications may be made to the embodiments described without departing from the spirit and scope of
30 the invention.

CLAIMS

1. A method of processing a sulphide mineral composition which at least partly comprises an iron containing mineral, the method comprising the steps of;
 - 5 (a) milling said composition to a particle size P80 of 20 microns or less,
 - (b) leaching said composition with a solution comprising sulphuric acid and ferric ions at ambient pressure whilst sparging with an oxygen containing gas in an open tank reactor at a temperature of up to about the boiling point of the solution, whereby at least some of the acid and at least some of the ferric ions are obtained from dissolution of the iron containing mineral, and ferrous ions generated by the leaching reaction are substantially re-oxidised to ferric ions in the leaching solution;
 - 10 (c) precipitating iron and separating said iron and solid materials from the leaching solution;
 - (d) extracting desired metal ions from the leaching solution by solvent extraction with an organic solvent to form an organic phase and raffinate comprising sulphuric acid and ferric ions;
 - 20 (e) returning the raffinate to the open leaching tank reactor and blending with further milled composition;
 - (f) separating the metals from the organic phase obtained in step (d) by stripping with electrolyte from an electrowinning cell and electrowinning.
2. The method of claim 1, wherein said composition is a flotation concentrate.
3. The method of claim 2, wherein said concentrate is a low grade concentrate.
- 30 4. The method of claim 1, wherein said iron containing mineral is a pyrite ore.
5. The method of claim 4, wherein said mineral composition comprises 20 to 60 wt% pyrite.
- 35 6. The method of claim 5, wherein substantially all of said ferric ions are generated by dissolution of pyrite.
7. The method of claim 1, wherein said composition

is milled to a particle size of P80 of 10 micron or less.

8. The method of claim 1, wherein said temperature is from about 60°C up to about the boiling point of the leaching solution.

5 9. The method of claim 1, wherein said gas is oxygen.

10. The method of claim 9, wherein oxygen is sparged at a rate of 400 to 1000kg per ton of metal produced.

10 11. The method of claim 1, wherein the solid from step (c) is further leached to recover any precious metals.

12. The method of claim 11, wherein said precious metals are selected from the group consisting of gold, platinum or silver.

15 13. The method of claim 1 or claim 2, wherein said metal is selected from the group consisting of copper, zinc, nickel or cobalt.

14. A method of processing a sulphide mineral composition comprising about 30 to about 40 wt% chalcopyrite, about 40 to about 50 wt% pyrite and up to 20wt% siliceous gangue, the method comprising

20 (a) milling the composition to a particle size P80 of 10 microns,

25 (b) leaching said composition with a solution comprising sulphuric acid and ferric ions at ambient pressure whilst sparging with oxygen at a rate of about 600kg per tonne of copper produced in an open reactor at a temperature of about 90°,

30 (c) neutralising the leaching solution with limestone to precipitate excess iron as goethite and removing the goethite and any other solids from the leaching solution;

(d) filtering the leaching solution and extracting dissolved copper from the leaching solution by solvent extraction with an organic solvent, such that the raffinate comprises sulphuric acid and ferric ions;

35 (e) returning the raffinate to the leaching tank and blending with further milled composition;

(f) separating the copper from the organic phase obtained in step (c) by stripping with electrolyte from an electrowinning cell and electrowinning.

15. A method of processing a sulphide mineral composition which at least partly comprises an iron containing mineral, the method comprising the steps of;

(a) milling said composition to a particle size P80 of 20 microns or less and

(b) leaching said composition with a solution comprising sulphuric acid and ferric ions at ambient pressure whilst sparging with an oxygen containing gas in an open tank reactor at a temperature of up to about the boiling point of the solution, whereby at least some of the acid and at least some of the ferric ions are obtained from dissolution of the pyrite, and ferrous ions generated by the leaching reaction are substantially re-oxidised to ferric ions in the leaching solution.

16. The method of claim 15 wherein said composition is a flotation concentrate.

17. The method of claim 15 wherein said iron containing mineral is a pyrite ore.

18. The method of claim 17 wherein said composition comprises 20 to 60 wt% pyrite.

19. The method of claim 18 wherein substantially all of said ferric ions are generated by dissolution of pyrite.

20. The method of claim 15 wherein said composition is milled to a particle size P80 of 5 micron.

21. The method of claim 15 wherein said temperature is about 60°C up to the boiling point of the leaching solution.

22. The method of claim 15 wherein said gas is oxygen.

23. The method of claim 22 wherein oxygen is sparged at a rate of about 400 to about 1000kg per tonne of metal produced.

24. The method of claim 15 wherein a surfactant is added in step (a) to minimise frothing of the solution.

25. A method of processing a metal sulphide flotation concentrate comprising the steps of;

(a) milling said ore to P80 of 5 micron and

5 (b) leaching said ore with a solution comprising sulphuric acid and ferric ions, at ambient pressure whilst sparging with an oxygen containing gas in an open tank reactor at a temperature of up to about the boiling point of the solution.

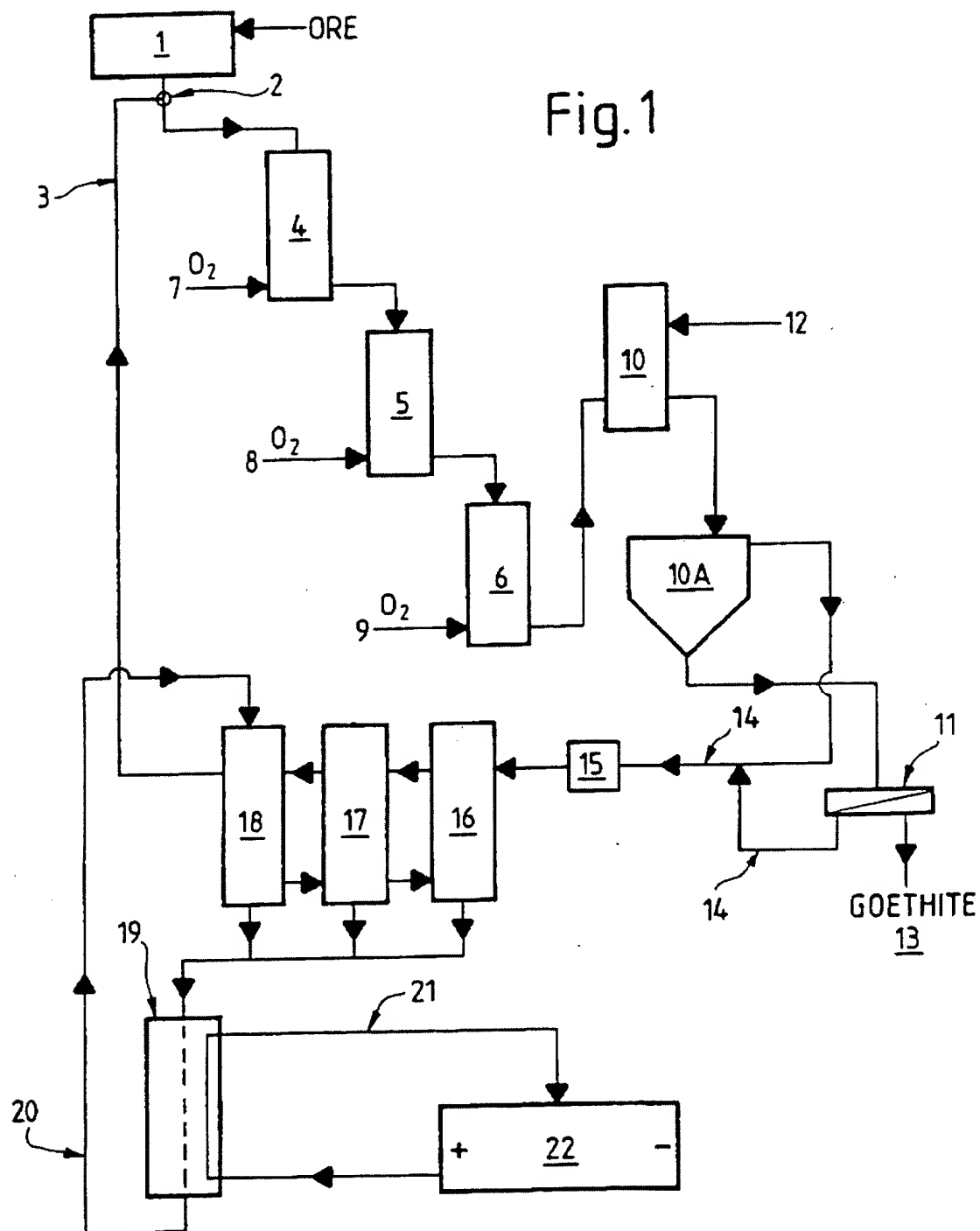
26. The method of claim 25 wherein said temperature
10 is about 60°C up to the boiling point of the leaching solution.

27. The method of claim 26 wherein said gas is oxygen.

28. The method of claim 27 wherein oxygen is
15 sparged a rate of about 400 to about 1000kg per tonne of metal produced.

29. The method of claim 28 wherein a surfactant is added in step (a) to minimise frothing of the solution.

Fig.1



INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 96/00157

A. CLASSIFICATION OF SUBJECT MATTER		
Int Cl ^o : C22B 3/08 19/02 11/00 23/00 15/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C22B 3/08 19/02 11/00 23/00 15/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU : IPC as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) JAPIO : Leach: pyrit: chalcopyrit: sulphide: sulfide: WPAT : Leach: pyrit: chalcopyrit: sulphide: sulfide:		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU 81941/87 A (ELECTROLYTIC ZINC COMPANY OF AUSTRALASIA LTD. 23 June 1988 Examples 2, 4	1-23, 25-28
X Y	US 3959436 A (WATTS), 25 May 1976 Column 2, line 19 - column 3, line 7	1-14, 20-23 & 25-28 15-19
Y	US 4004991 A (VELTMAN et al.), 25 January 1977 Example 1	1-23, 25-28
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 16 May 1996		Date of mailing of the international search report 23rd May 1996.
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (06) 285 3929		Authorized officer SUDATH KUMARASINGHE Telephone No.: (06) 283 2269

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 96/00157

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4571262 A (KERFOOT et al.), 18 February 1986 Column 2, line 53 - column 3, line 3 and column 5, lines 22-26	1-14, 20-23 & 25-28
Y	US 3951649 A (KIESWETTER et al.), 20 April 1976 Column 1, line 54 - column 2, line 3	1-8, 11-21 & 25-26
A	GB 2108480 A (SHERRITT GORDON MINES LTD.), 18 May 1983 The whole document	1-29

Form PCT/ISA/210 (continuation of second sheet) (July 1992) coplin

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.

PCT/AU 96/00157

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
AU	81941/87	EP ES	272060 2005483	FI JP	875580 63166935	NO	875294
US	3959436	CA	1062472				
US	4004991	AU DK ES FI FR ZA	18890/76 4762/76 452614 763006 2328775 7606135	JP MX NL SE YU	52066818 143151 7611752 7611751 2563/76	BE BR CA DE GB	847511 7607062 1049953 2746601 1494990
US	4571262	AU ZA	48777/85 8508068	NO	854233	CA	1234289
US	3951649						
GB	2108480	AU ZA	88583/82 8207078	FR	2515688	CA	1173655

END OF ANNEX